Molecular Structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$, a Model for Ligand Exchange between Te(IV) Centers

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$ClTe(O^iPr)_3$ could be prepared from stoichiometric amounts of $TeCl_4$ and $Te(O^iPr)_4$, a reaction that requires the exchange of ligands between different Te centers. Ligand redistribution between telluranes was studied, and rapid exchange of −Cl and −OR (R = Me, ^{i}Pr) ligands in solutions of several binary mixtures of $Te(OMe)_4$, $Te(O^iPr)_4$, $ClTe(OMe)_3$, and $ClTe(O^iPr)_3$ was established by multinuclear NMR spectroscopy. The solid-state structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$, the first structurally characterized adduct between different telluranes, was investigated by single-crystal X-ray diffraction. It exhibits a very short Te−O···Te bridge between the two Te centers and additional Te···O and Te···Cl contacts between different adduct molecules. Selected structural parameters of $Te(OMe)_4 \cdot ClTe(OMe)_3$ are Te1−Cl1 274.6(3), Te1−O13 191.0(5), Te1−O12 194.9(6), Te1−O11 200.9(7), Te1···O24 226.8(5), Te1···O11a 314.2(8), Te2−O21 191.6(5), Te2−O22 198.7(5), Te2−O23 190.1(5), Te2−O24 225.3(5), Te2···O13 307.8(6), and Te2···O22b 269.2(6) pm and Te2−O24···Te1 126.1(2)°. Ab initio (MP2/LANL2DZP) geometry optimization of the model compound $Te(OH)_4 \cdot ClTe(OH)_3$ revealed that the central Te−O···Te bridge is less symmetric and hence weaker in the isolated adduct molecule than in the solid state. The stability of $Te(OMe)_4 \cdot ClTe(OMe)_3$ toward decomposition in $Te(OMe)_4$ and $ClTe(OMe)_3$ is attributed to the strengths of the short Te−O···Te bridge between $Te(OMe)_4$ and $ClTe(OMe)_3$. On the basis of the molecular structures of $Te(OH)_4 \cdot ClTe(OH)_3$ and $Te(OMe)_4 \cdot ClTe(OMe)_3$, a mechanism for the exchange of −OR groups between Te(IV) centers is proposed.

Introduction

The coordination chemistry of Te(IV) compounds recently gained interest,[1] not least due to the immunomodulatory activity of ammonium trichloro(dioxyethylene-*O,O′*)tellurate.[2,3] Many molecular and crystal structures of Te(IV) compounds exhibiting *intra*molecular donor−acceptor interactions have so far been reported.[4−7] In the solid state, Te(IV) compounds containing at least one Te−O or Te−X (X = Cl, Br, I) bond also form *inter*molecular donor−acceptor interactions via the O or X atoms, leading to molecular dimers,[3,8−10] oligomers,[11−13] or chains.[14]

Dynamic aspects of the coordination chemistry of Te(IV) compounds were studied via NMR spectroscopy.[15] The presence of a Lewis acidic site in combination with a quick and easy exchange of ligands *in solution* is a feature exhibited by compounds that act as homogeneous catalysts.[16] A closer look at the ligand exchange reactions and the donor−acceptor interactions in telluranes is thus of interest to evaluate a potential catalytic activity.

Results and Discussion

Synthesis. For the known compound $ClTe(O^iPr)_3$,[17] a new synthesis was found by reacting stoichiometric amounts of $TeCl_4$ and $Te(O^iPr)_4$, respectively, in THF solution, while $ClTe(OMe)_3$ was successfully synthesized from equal amounts of $Te(OMe)_4$ and acetyl chloride. By NMR spectroscopy, we discovered that the reaction mixture can be kept at room temperature to obtain the products. They precipitated either on cooling or on slowly evaporating the solvent. $Te(OMe)_4 \cdot ClTe(OMe)_3$ (**1**) (Figure 1) was obtained from an approximately equimolar solution of $Te(OMe)_4$ and $ClTe(OMe)_3$ in $CDCl_3$, which was used as a sample for NMR spectroscopic studies of exchange reactions. Complexes between Te(IV) compounds and typical Lewis bases are known, e.g., $TeCl_2(OPh)_2 \cdot bipy$,[18] but **1** is the first example of an adduct between two differently substituted Te(IV) compounds.

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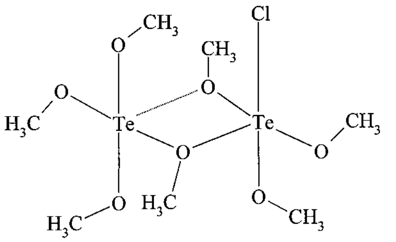

Figure 1. Structural formula of $Te(OMe)_4 \cdot ClTe(OMe)_3$.

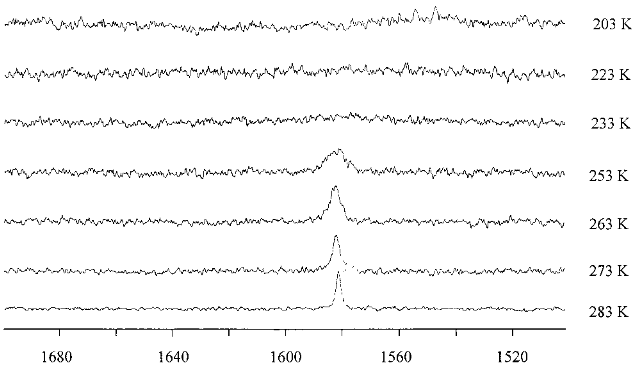

Figure 2. ^{125}Te VT NMR spectra of a mixture of $Te(O^iPr)_4$ (0.247 mmol) and $ClTe(O^iPr)_3$ (0.144 mmol) in CD_2Cl_2.

Table 1. ^1H and ^{125}Te NMR Chemical Shifts of Binary Mixtures of $Te(OMe)_4$ and $Te(O^iPr)_4$ in $CDCl_3$[a]

x_{OMe}	$\delta(OCH_3)$	$\delta(OCH(CH_3)_2)$	$\delta(OCH(CH_3)_2)$	$\delta(Te)$
0.000		1.18	4.23	1538.4
0.138	3.53	1.07	4.39	1531.9
0.264	3.60	1.14	4.47	1530.2
0.314	3.62	1.15	4.50	1529.4
0.581	3.67	1.19	4.49	1523.8
0.957	3.69	1.20	4.46	1518.8
1.000	3.71			1519.2

[a] x_{OMe} represents the molar fraction of $Te(OMe)_4$ in the binary $Te(OMe)_4/Te(O^iPr)_4$ mixture.

NMR Spectroscopy. Ligand exchange has already been established between alkoxytelluranes $Te(OR)_4$ and alcohols HOR′.[15] NMR experiments should elucidate dynamics of ligand exchange between different telluranes. For this purpose, NMR spectra of $CDCl_3$ solutions containing two tetraalkoxytelluranes, $Te(OR)_4$ and $Te(OR')_4$ (R, R′ = Me, ^iPr) (Table 1), or containing a tetraalkoxytellurane and a chlorotrialkoxytellurane, $Te(OR)_4$ and $ClTe(OR)_3$ (R = Me, ^iPr), were investigated.

All ^{125}Te NMR spectra of binary mixtures of $Te(OMe)_4$ and $Te(O^iPr)_4$ show only a single signal at room temperature, indicating a rapid exchange of −OMe and $-O^iPr$. ^1H NMR spectra of mixtures of $Te(OMe)_4$ and $ClTe(OMe)_3$ as well as $Te(O^iPr)_4$ and $ClTe(O^iPr)_3$ exhibit only a single set of signals for the methyl and isopropyl groups; hence, a rapid exchange of alkoxy groups can be inferred as well. As only a single signal is present in the ^{125}Te NMR spectra of the same mixtures at room temperature, alkoxy and chlorine groups must also quickly exchange with each other.[19] ^{125}Te VT NMR spectra (see Figure 2) support this interpretation as the single signal which is very sharp at room temperature becomes broader at lower temperatures. It was too broad to be observed between 233 and 223 K, whereas at 203 K the very broad signal for $Te(O^iPr)_4$ emerged between 1580 and 1520 ppm.

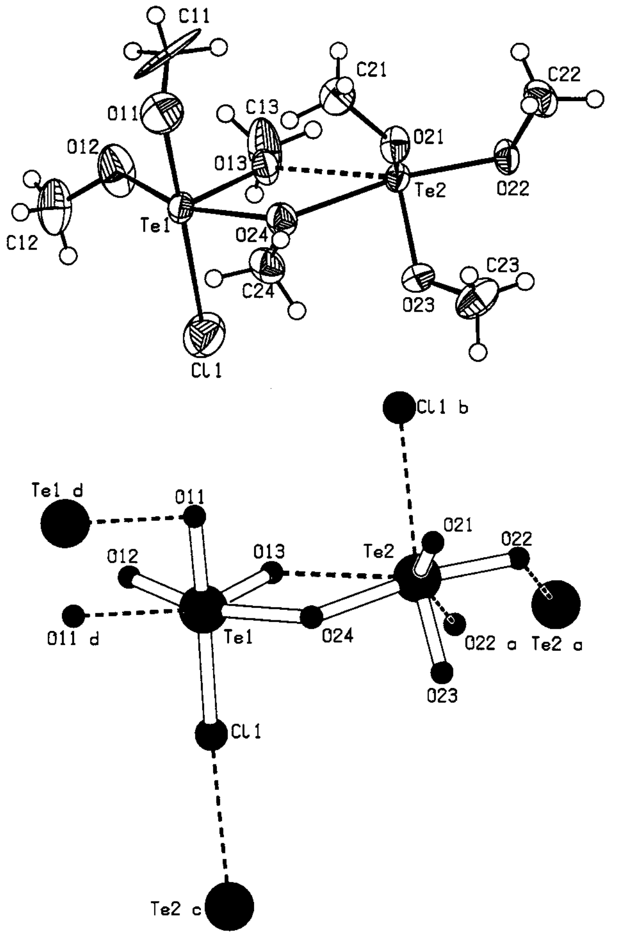

Figure 3. (a, top) Molecular structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$ in the solid state. Displacement ellipsoids are at the 50% probability level. (b, bottom) Coordination mode of the Te atoms in $Te(OMe)_4 \cdot ClTe(OMe)_3$, including intermolecular contacts. Only Te, O, and Cl atoms are shown.

The rapid redistribution of −OR ligands, either between $Te(OR)_4$ and HOR′ or between $Te(OR)_4$ and $Te(OR')_4$, is in contrast to the rather slow exchange of −SR ligands between $Te(SR)_2$ and HSR′ or between $Te(SR)_2$ and $Te(SR')_2$ that was reported recently.[20] The difference between $Te(OR)_4$ and $Te(SR)_2$ can be rationalized in terms of a stronger Lewis acidity of the former, which leads, e.g., to intermolecular secondary bonds in all solid-state structures of $Te(OR)_4$ and related compounds known so far (vide infra).

XRD Crystal and Molecular Structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$ and MP2/LANL2DZP Optimized Molecular Structure of $Te(OH)_4 \cdot ClTe(OH)_3$. The molecular structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$ in the solid state is given in Figure 3; selected structural parameters are given in Table 2.

Comparison of the MP2/LANL2DZP optimized structures of $Te(OH)_4$ and $ClTe(OH)_3$ with that of $Te(OH)_4 \cdot ClTe(OH)_3$ reveals structural changes due to adduct formation, while comparison of the structure of $Te(OH)_4 \cdot ClTe(OH)_3$ with that of $Te(OMe)_4 \cdot ClTe(OMe)_3$ shows the impact of the different phases, i.e., "isolated molecule" and solid state, on the molecular structure.

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(19) In spite of the precautions taken (see the General Procedures in the Experimental Part), it cannot be excluded that traces of HOR and HCl due to hydrolysis of the telluranes are present, which might catalyze the exchange of −OR and −Cl, respectively. Anyhow, the single-crystal XRD structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$ (see later in the text) gives a hint to an exchange mechanism that does not rely on the presence of HOR or HCl.

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Table 2. Selected Structural Parameters (Atomic Distances in Picometers, Angles in Degrees) from MP2/LANL2DZP Optimized Geometries of $Te(OH)_4$ (C_2), $ClTe(OH)_3$ (C_s), and $Te(OH)_4 \cdot ClTe(OH)_3$ (C_1) and the XRD Geometry of $Te(OMe)_4 \cdot ClTe(OMe)_3$

	$Te(OH)_4$	$ClTe(OH)_3$	$Te(OH)_4 \cdot ClTe(OH)_3$	$Te(OMe)_4 \cdot ClTe(OMe)_3$
Te1−Cl1		252.2	254.5	274.6(3)
Te1−O11		193.1	198.9	200.9(7)
Te1−O12		192.3	194.7	194.9(6)
Te1−O13		192.3	194.5	191.0(5)
Te1···O24			241.2	226.8(5)
Te1···O11a				314.2(8)
Te2−O21	194.0		190.5	191.6(5)
Te2−O22	199.5		197.7	198.7(5)
Te2−O23	194.0		193.9	190.1(5)
Te2−O24	199.5		209.6	225.3(5)
Te2···O13			301.8	307.8(6)
Te2···O22b				269.2(6)
Cl1−Te1−O11		166.3	160.8	177.5(2)
Cl1−Te1−O12		84.1	85.1	89.2(3)
Cl1−Te1−O13		84.1	81.9	86.4(2)
Cl1−Te1···O24			110.1	97.0(2)
O11−Te1−O12		87.2	82.4	88.3(4)
O11−Te1−O13		87.2	85.0	93.1(3)
O12−Te1−O13		101.1	96.0	87.7(3)
O12−Te1···O24			159.0	160.3(3)
O21−Te2−O22	90.0		83.9	87.4(2)
O21−Te2−O23	109.5		103.4	93.8(2)
O22−Te2−O23	90.0		86.4	88.9(2)
O22−Te2−O24	156.8		160.2	166.1(2)
O13−Te1···O24			72.3	74.2(2)
Te2−O24···Te1			122.0	126.1(2)
Te2−O24−Te1O13			20.9	3.9(3)

[a] Numbering of the atoms according to Figure 3. MP2/LANL2DZP atomic distances refer to an r_e structure.

Table 3. Crystal Data for $Te(OMe)_4 \cdot ClTe(OMe)_3$[a]

empirical formula	$C_7H_{21}O_7ClTe_2$	α/deg	99.975(7)
fw	507.9	β/deg	99.750(7)
cryst syst	triclinic	γ/deg	91.667(7)
space group	$P1$	V/Å^3	763.3(1)
Z	2	no. of reflns measd	4121
λ/**Å**	0.710 73	no. of unique reflns	3314
temp/K	203	m/mm^{-1}	4.01
ρ_{calcd}/g cm^{-3}	2.210	refln $\lvert F\rvert > 4\sigma(F)$	2377
a/Å	7.1309(6)	R1 [$\lvert F\rvert > 4\sigma(F)$]^a	0.0455
b/Å	10.3345(8)	wR2^b	0.1116
c/Å	10.6899(8)	GOF on F^2	1.042

[a] $R1 = \sum\lvert\lvert F_o\rvert - F_c\rvert/\sum\lvert F_o\rvert$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2\}^{1/2}$.

$Te(OMe)_4 \cdot ClTe(OMe)_3$ is the first structurally characterized compound with a Te−O(R)···Te bridge between differently substituted Te atoms. Te2−O24···Te1 represents so far the shortest Te−O(R)−Te bridge, with the distances Te2−O24 and Te1···O24 being nearly equal in the solid state (see for comparison, e.g., the solid-state structures of tellurium(IV) catecholate,[21] or tellurium(IV) tetramethylglycolate[22]). The symmetry index $s = [d(Te\cdots O) - d(Te{-}O)]/[d(Te\cdots O) + d(Te{-}O)]$ can be taken as a geometric measure for the symmetry and hence the ionic character of a Te−O···Te bridge.[23] Furthermore, if the sum of the distances, $d(Te\cdots O) + d(Te{-}O)$, is similar for different bridges, their strengths can be compared by s. The smaller the difference between $d(Te\cdots O)$ and $d(Te{-}O)$, the smaller is s and the more ionic is the character of the bridge. If $d(Te\cdots O)$ and $d(Te{-}O)$ differ significantly, the latter can be regarded as a normal covalent bond, while the former represents a weak secondary interaction. Thus, for comparable sums of $d(Te\cdots O)$ and $d(Te{-}O)$, the bridge with the higher ionic character is the stronger one. For Te1···O24−Te2 in **1**, s is calculated as 3.3×10^{-3}, while for Te···O−Te bridges in tellurium(IV) catecholate,[21] tellurium(IV) tetramethylglycolate,[22] trichloro(ethane-1,2-diolate-*O,O′*)tellurate(IV),[24] and 2,2′-biphenylylene-2-biphenylylphenoxytellurane,[25] values of 0.112, 0.208, 0.168, and 4.5×10^{-3}, respectively, are obtained. Thus, from the small sum of the distances Te2−O24 and Te1···O24 and the high symmetry of the Te1···O24−Te2 fragment, a high strength of the bridge can be inferred.

Apart from Te2−O23, the sequence of the Te−O bond lengths is the same for the solid-state structure of **1** and the ab initio optimized molecular structure of $Te(OH)_4 \cdot ClTe(OH)_3$. The axial bond Te2−O24 is significantly longer than the other covalent Te−O bonds; i.e., it is weakened by the strong interaction between O24 and Te1, the shortest dative O → Te(IV) bond known so far.[26] Furthermore, the sum of the bonding angles around O24 is 359.5°, giving a nearly planar Te_2OC arrangement. In the isolated adduct $Te(OH)_4 \cdot ClTe(OH)_3$, Te2−O24 is shorter (209.6 pm) and Te1···O24 longer (241.2 pm) than in **1** (225.3 and 226.8 pm, respectively), thus implying that the Te−O···Te bridge is less symmetrical and thus weaker ($s = 7.0 \times 10^{-2}$, vide infra) than in the solid state. We tend to attribute these differences of the Te−O···Te bridge in the two cases to the different abilities of their molecular environments to stabilize charge separations. Due to the polar environment of the solid state and additional intermolecular contacts, stabilization of an ionic bridge is much easier to accomplish for $Te(OMe)_4 \cdot ClTe(OMe)_3$ than for the model compound $Te(OH)_4 \cdot ClTe(OH)_3$, and hence a more symmetric Te−O···Te bridge is feasible for it. The Te2−O24···Te1−O13 torsion is in both cases close to the eclipse of Te2−O24 and Te1−O13, thus allowing a maximum of interaction between Te2 and O13. For the bridge Te1−O13···Te2, s is calculated as 0.234, rendering it obviously weaker than Te2−O24···Te1. From the geometry of the Te−O···Te bridges it is furthermore inferred that $ClTe(OMe)_3$ is a stronger Lewis acid than $Te(OMe)_4$ since it forms a distinctly shorter Te···O bond than the latter. In this respect, it is noteworthy that not a Te−Cl bond but a Te−O bond is trans to Te1···O24.

On the basis of the molecular structures of $Te(OMe)_4 \cdot ClTe(OMe)_3$ and $Te(OH)_4 \cdot ClTe(OH)_3$, a mechanism for the exchange of alkoxy groups between different Te(IV) centers is proposed (see Scheme 1).

In the solid state, additional Te···O interactions lead to chains of $Te(OMe)_4 \cdot ClTe(OMe)_3$ units, the chains being linked to each other by Te···Cl contacts. In the solid state the bond angles at Te1 become close to 90° and 180°, respectively, reflecting the reduced repulsion of the lone pair on the other bonds of Te1.

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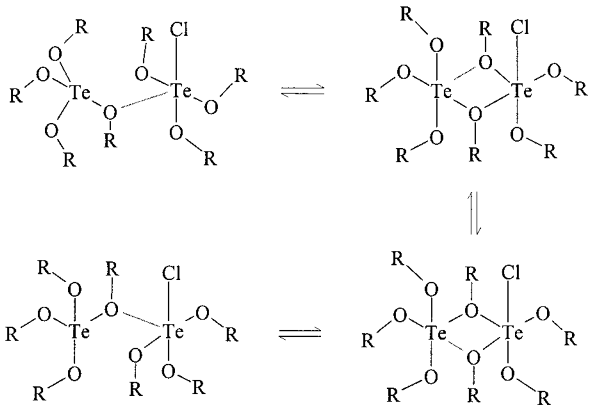
Scheme 1. Proposed Mechanism for the Exchange of Alkoxy Groups between $Te(OR)_4$ and $ClTe(OR)_3$



This effect is attributed to the intermolecular Te···O contacts in the solid state, by which Te1 reaches a coordination number of 6 (see Figure 3b), with a slightly distorted octahedral configuration. Te1···O11a slightly increases Te1−O11, while the Te2···O22b and Te2···Cl1 contacts significantly narrow O21−Te2−O23 and slightly increase Te2−O22. The configuration of Te2 is best described as tricapped ψ trigonal bipyramidal. The coordination of the Te atom in $Te(OH)_4$ (C_2 symmetry) can be described as ψ trigonal bipyramidal, with O22 and O24 being in apical positions and O21, O23, and the lone pair in equatorial positions. In accordance with the VSEPR rule, bonds to the apical ligands are longer than those to the equatorial ones. In $ClTe(OH)_3$ (C_s symmetry), the coordination of the Te atoms is distorted pseudo trigonal bipyramidal, as can be seen from the bonding angles. Considering the lengths of the Te−O bonds, there is hardly any difference between the equatorial and the axial ones, a fact attributed to the smaller trans effect of Cl compared to O.

The impact of formation of $Te(OH)_4{\cdot}ClTe(OH)_3$ from $Te(OH)_4$ and $ClTe(OH)_3$ on their molecular structures is less dramatic than the changes of the adduct between the isolated molecule and the solid state, as can be seen from Table 2. Intermolecular interactions are responsible for Te1−Cl1 being longer in $Te(OMe)_4{\cdot}ClTe(OMe)_3$ than in $Te(OH)_4{\cdot}ClTe(OH)_3$. MP2/LANL2DZP thermochemical calculations for the formation of $Te(OH)_4{\cdot}ClTe(OH)_3$ from $Te(OH)_4$ and $ClTe(OH)_3$, corrected for the basis set superposition error by counterpoise calculations, gave values of $\Delta H^{298} = -46.4$ and $\Delta G^{298} = +3.7$ kJ mol^{-1}, confirming the strength of the Te2−O24···Te1 bridge in the adduct but also indicating substantial dissociation of the adduct in the gas phase.

Conclusion

Tetraalkoxy- and chlorotrialkoxytelluranes exchange −OR and −Cl ligands with each other. At room temperature this reaction proceeds fast on the NMR time scale. This facile exchange can be used for synthetic purposes.

The adduct $Te(OMe)_4{\cdot}ClTe(OMe)_3$ owes its existence to a very strong Te−O···Te bridge. Comparison of solid-state and ab initio optimized molecular structures reveals a higher symmetry for this bridge in the former, due to an increased stabilization of its ionic character in a polar environment. The symmetry index, $s = [d(\mathrm{Te}\cdots\mathrm{O}) - d(\mathrm{Te{-}O})]/[d(\mathrm{Te}\cdots\mathrm{O}) + d(\mathrm{Te{-}O})]$, proved to be a useful geometric measure to compare the strengths of Te−O···Te bridges. On the basis of the different geometries of the Te−O···Te bridges in the solid state and in the isolated molecule, a pathway for the exchange of −OR groups between Te(IV) centers could be suggested.

Experimental Part

General Procedures. All procedures involving $TeCl_4$, $Te(OR)_4$, and $ClTe(OR)_3$ were carried out under an inert gas atmosphere or in a vacuum, using carefully dried glassware and solvents purified according to standard procedures. NMR: Bruker DRX 400, $B_1(^1H) = 400.0$ MHz, $B_1(^{13}C) = 100.577$ MHz, $B_1(^{125}Te) = 126.387$ MHz. Standard: TMS (^1H, ^{13}C) and $Te(CH_3)_2$ (^{125}Te). CH analysis was performed with an Elemental Vario EL2. $Te(OMe)_4$ and $Te(O^iPr)_4$ were prepared from $TeCl_4$ and the appropriate sodium alcoholates, according to literature procedure.[27]

$ClTe(O^iPr)$. $Te(O^iPr)_4$ (10.96 g, 30.1 mmol) and $TeCl_4$ (2.67 g, 9.9 mmol) were mixed in 40 mL of THF and stirred for 24 h. The solution was concentrated by evaporating THF in vacuo and then cooled to −40 °C, and the precipitate formed was washed with cold diethyl ether and dried in vacuo. Yield: 12.62 g, 93.6%. ^1H NMR: $\delta = 5.04$ (m, 1H, $-OCH(CH_3)_2$), 1.27 (d, $^3J(H,H) = 6.0$ Hz, $^1J(^{13}C,^1H) = 127$ Hz, 6H, $-OCH(CH_3)_2$). ^{13}C NMR: $\delta = 70.8$ ($-OCH(CH_3)_2$), 25.7 ($-OCH(CH_3)_2$). ^{125}Te NMR: $\delta = 1634.6$.

$ClTe(OMe)_3$. Acetyl chloride (1.00 g, 12.7 mmol) was added to a stirred solution of $Te(OMe)_4$ (3.20 g, 12.7 mmol) in 30 mL of THF. All volatile compounds were subsequently removed in vacuo, leaving a white solid, from which $ClTe(OMe)_3$ was obtained by recrystallization from chloroform. Yield: 2.88 g, 88.5%. ^1H NMR: $\delta = 4.02$ (s). ^{13}C NMR: $\delta = 53.6$. ^{125}Te NMR: $\delta = 1586$.

$Te(OMe)_4{\cdot}ClTe(OMe)_3$. $Te(OMe)_4$ (95 mg, 0.38 mmol) and $ClTe(OMe)_3$ (103 mg, 0.40 mmol) were dissolved in 0.5 mL of $CDCl_3$. On cooling to −20 °C, colorless crystals of $Te(OMe)_4{\cdot}ClTe(OMe)_3$, suitable for crystal structure analysis, precipitated. ^1H NMR: $\delta = 3.86$ (s). ^{13}C NMR: $\delta = 52.5$. ^{125}Te NMR: $\delta = 1556.3$. Anal. Calcd for $C_7H_{21}ClO_7Te_2$ (fw = 507.90): C, 16.55; H, 4.17. Found: C, 16.19; H, 3.74.

Crystal Structure Determination. The crystal structure data were collected on a Siemens-P4 diffractometer, the structure was solved by direct methods and a difference Fourier technique (SIR),[28] and structural refinement was against F^2 (SHELXL-97).[29] Details of the crystal structure determination and the crystal data of $Te(OMe)_4{\cdot}ClTe(OMe)_3$ are given in Table 3.

Theoretical Methods. The ab initio calculations were performed on various servers of the Zentrum für Datenverarbeitung, Universität Mainz, using the GAUSSIAN94 software package.[30] A second-order perturbation calculation according to the theory of Møller and Plesset (MP2) followed the Hartree−Fock (HF) studies to account for the effects of dynamic electron correlation.[31] With both levels an effective core double-ζ valence basis set according to Hay and Wadt[32] augmented by appropriate polarization functions for Te, Cl, and O (HF/LANL2DZP and MP2/LANL2DZP) was used.[33] At the HF level, all stationary points were characterized by numerical calculation of frequencies from first

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derivatives. Thermal corrections for H and G for all molecules in the present study were obtained at that level. The starting geometry of $Te(OH)_4 \cdot ClTe(OH)_3$ was generated from the XRD structure of $Te(OMe)_4 \cdot ClTe(OMe)_3$ by eliminating all H atoms and subsequently changing all the C atoms to H atoms. Geometry optimizations of $Te(OH)_4$ (C_2) and $ClTe(OH)_3$ (C_s) started from standard bond lengths and angles. Finally, counterpoise calculations were performed to account for the basis set superposition error in calculating the energies of adduct formation of $Te(OH)_4 \cdot ClTe(OH)_3$ from $Te(OH)_4$ and $ClTe(OH)_3$.[34,35]

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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